In memory of S. M. Nelson

Nickel(II), Copper(II), and Zinc(II) Complexes of Penta-azamacrocyclic Ligands. Crystal and Molecular Structure of 3,6,9,12-Tetramethyl-3,6,9,12,18-penta-azabicyclo[12.3.1]octadeca-1(18),14,16-trienezinc(II) Perchlorate†

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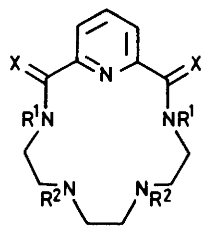
The three related penta-azamacrocyclic ligands 6,9-dimethyl-2,13-dioxo-3,6,9,12,18-penta-azabicyclo[12.3.1]octadeca-1(18),14,16-triene (L^1), 6,9-dimethyl-3,6,9,12,18-penta-azabicyclo-[12.3.1]octadeca-1(18),14,16-triene (L^2), and 3,6,9,12-tetramethyl-3,6,9,12,18-penta-azabicyclo[12.3.1]octadeca-1(18),14,16-triene (L^3), have been prepared. The complexes $[M(L)(dmso)][ClO_4]_2$ (dmso = dimethyl sulphoxide; L = L^2, M = Ni or Zn; L = L^3, M = Ni) and $[M(L)][ClO_4]_2$ (L = L^2, M = Cu; L = L^3, M = Cu or Zn) have been isolated. The Ni^{2+} complexes are high-spin and six-co-ordinate, and the Cu^{2+} complexes five-co-ordinate. ^{13}C N.m.r. spectroscopy shows $[Zn(L^2)(dmso)][ClO_4]_2$ to be a 2:1 mixture of two species, one symmetric and the other asymmetric, whilst in $[Zn(L^3)][ClO_4]_2$ only *ca.* 10% of the asymmetric species is present in nitromethane solution. *X*-Ray crystallography has been used to dermine the structure of the symmetric isomer of $[Zn(L^3)][ClO_4]_2$ {R = 0.039 for 1 816 observed [$I/\sigma(I) \geqslant 3.0$] diffractometer collected reflections}; it reveals distorted trigonal-bipyramidal geometry about the zinc ion, and an approximate C_2 rotation axis passing through the zinc and pyridine N atoms, and bisecting the macrocyclic C–C bond furthest removed from the pyridine ring [Zn–N 1.999(4)—2.252(5) Å].

Most syntheses of pyridyl-containing penta-azamacrocycles have involved the use of a template metal ion to achieve cyclisation. Although attempts to prepare macrocyclic Schiff-base complexes by condensing 2,6-diacetylpyridine with diamines such as $(NH_2CH_2CH_2XCH_2-)_2$ (X = NH, O, or PPh) in the presence of template metal ions such as Ni^{2+} and Cu^{2+} were unsuccessful,[1] successful template syntheses have been achieved using other metal ions (*e.g.* Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag^{+}, Pb^{2+}, and Sn^{4+}).[2–6] Busch and co-workers[6] succeeded in obtaining the saturated penta-azamacrocycle L^4 by reducing the Mn^{2+} complex of the corresponding Schiff-base macrocycle with nickel–aluminium alloy in aqueous base. Our attempts to prepare the corresponding macrocycle L^5, in an analogous way starting from pyridine-2,6-dicarbaldehyde and $(NH_2CH_2CH_2NHCH_2-)_2$, gave very low yields (5—10%). Therefore, a better route to 15-membered ring penta-azamacrocycles was sought.

In this paper we report the synthesis of three related penta-azamacrocycles, L^1—L^3, beginning with the high-dilution technique to prepare the diamide macrocycle L^1. Although this route gives only moderate yields (*ca.* 24%), the starting materials are relatively cheap and readily available. Furthermore, L^1 can be reduced in tetrahydrofuran (thf) solution with BH_3·thf to give good yields of L^2, and L^2 is readily converted to L^3 in very good yield by reaction with a mixture of formaldehyde and formic acid. The Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes of L^2 and L^3 have been isolated, characterised by elemental analyses, fast atom bombardment (f.a.b.) mass spectrometry, and by ^{13}C n.m.r. for the diamagnetic Zn^{2+} complexes. The Ni^{2+} and Cu^{2+} complexes were investigated further by u.v.–visible spectroscopy and magnetic moment measurements. The crystal and molecular structure of $[Zn(L^3)][ClO_4]_2$ is also reported.



L^1; X = O; R^1 = H, R^2 = Me
L^2; X = H_2; R^1 = H, R^2 = Me
L^3; X = H_2; R^1 = R^2 = Me
L^4; X = Me, H; R^1 = R^2 = H
L^5; X = H_2; R^1 = R^2 = H

Experimental

Materials.—Dry toluene was obtained by refluxing over CaH_2 for 20 h followed by distillation under dry dinitrogen. Pyridine-2,6-dicarboxylic acid dichloride was prepared from pyridine-2,6-dicarboxylic acid (20 g; Aldrich) by refluxing overnight under dry dinitrogen with excess thionyl chloride (100 g). Most of the excess thionyl chloride was removed by rotary evaporation; to remove the last traces the residue was dissolved in dry toluene (20 cm³) before removal by rotary evaporation. This procedure was repeated four more times, and the solid residue then transferred to a dry-box where it was stirred with dry light petroleum (50 cm³, b.p. 40—60 °C) for 15

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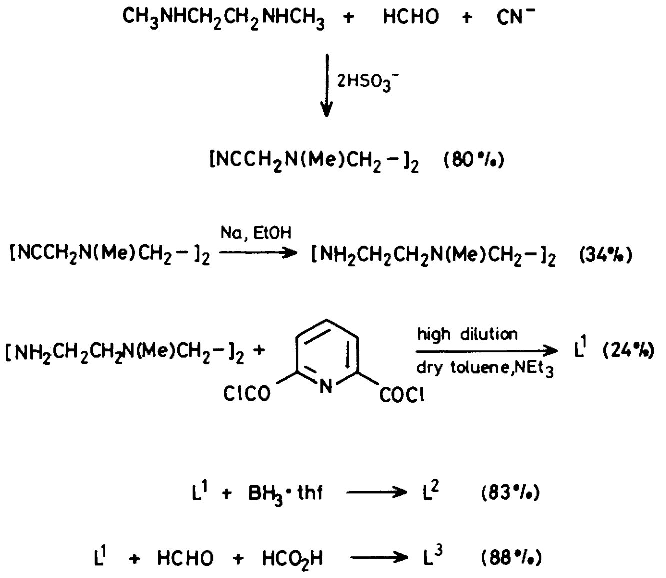
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: mmHg = 133 Pa.

Table 1. Metal complexes of L^2 and L^3 and their elemental analyses*

Complex	Colour	Recrystallised from CH_3NO_2–EtOH–Et_2O	Yield (%)	Formula	Analysis (%) C	H	N
$[Ni(L^2)(dmso)][ClO_4]_2$	Green	1:1:2	60	$C_{17}H_{33}Cl_2N_5NiO_9S$	33.8 (33.3)	5.2 (5.4)	11.8 (11.4)
$[Cu(L^2)][ClO_4]_2$	Blue-green	1:2:1	69	$C_{15}H_{27}Cl_2CuN_5O_8$	33.1 (33.4)	5.0 (5.0)	12.8 (13.0)
$[Zn(L^2)(dmso)][ClO_4]_2$	White		48	$C_{17}H_{33}Cl_2N_5O_9SZn$	32.9 (32.9)	5.1 (5.4)	11.6 (11.3)
$[Ni(L^3)(dmso)][ClO_4]_2 \cdot H_2O$	Green		53	$C_{19}H_{39}Cl_2N_5NiO_{10}S$	34.9 (34.6)	5.9 (6.0)	10.8 (10.6)
$[Cu(L^3)][ClO_4]_2$	Blue	1:1:2	59	$C_{17}H_{31}Cl_2CuN_5O_8$	35.8 (36.0)	5.6 (5.5)	12.2 (12.3)
$[Zn(L^3)][ClO_4]_2$	White		64	$C_{17}H_{31}Cl_2N_5O_8Zn$	36.4 (35.8)	5.7 (5.5)	11.9 (12.3)

* Calculated values are given in parentheses.



Scheme.

min, filtered off, and washed with more light petroleum (3 × 10 cm^3) to give the product (21.2 g, 87%). The purity was confirmed by ^1H n.m.r. spectroscopy. All other chemicals were reagent-grade commercial materials which were used without purification.

Spectra.—Proton-decoupled ^{13}C n.m.r. spectra were obtained at 45.28 MHz with a Bruker WH180 Fourier-transform (F.t.) n.m.r. spectrometer, and ^1H n.m.r. spectra at 220 MHz with a Perkin-Elmer R34 continuous-wave instrument. Chemical shifts are reported on the δ scale relative to $SiMe_4$ at $\delta = 0$. Infrared, u.v.–visible, and mass spectra were obtained with Perkin-Elmer 580B, Shimadzu 365, and Kratos MS80 spectrometers respectively.

Analyses and Other Procedures.—Microanalyses were obtained commercially. Analytical data are given in Table 1. Magnetic moments for powder samples of the complexes were obtained at room temperature with a Johnson-Matthey (Evans) magnetic susceptibility torsion balance. *X*-Ray data were collected with a Syntex $P2_1$ four-circle diffractometer, and analysed with SHELXTL[7] on a Data General DG30 computer.

Preparations.—The synthetic routes are outlined in the Scheme.

Preparation of $[NCCH_2N(Me)CH_2–]_2$. Sodium metabisulphite (46 g, 242 mmol) was dissolved in water (100 cm^3) and 37% aqueous formaldehyde (34 cm^3) added. The solution was boiled for 10 min, then cooled to room temperature, and *N,N'*-dimethyl-1,2-diaminoethane (20 g, 227 mmol) added with vigorous stirring. After 4 h, a solution of sodium cyanide (25 g, 510 mmol) in water (50 cm^3) was added. The mixture was left to stir overnight, whereupon a solid formed which was extracted with dichloromethane (4 × 100 cm^3). The combined extracts were dried with anhydrous $MgSO_4$, filtered, and the solvent removed with a rotary evaporator to leave a pale yellow solid. This was stirred with diethyl ether (200 cm^3), filtered off, and washed with more ether (3 × 20 cm^3) to leave a white solid, 1,6-dicyano-2,5-dimethyl-2,5-diazahexane (30 g, 181 mmol, 80% yield), m.p. 79—80 °C. ^1H N.m.r. ($CDCl_3$): 2.40 (6 H, s), 2.63 (4 H, s), and 3.64 p.p.m. (4 H, s); ^{13}C n.m.r. ($CDCl_3$): 42.25 (2 C, N-CH_2–CH_2), 45.24 (2 C, NMe), 52.90 (2 C, CH_2–CN), and 114.64 p.p.m. (2 C, CN). Electron-impact mass spectrum (Found: *m/z* 166; calc. for M^+, 166).

Preparation of $[NH_2CH_2CH_2N(Me)CH_2–]_2$. A slurry of $[NCCH_2N(Me)CH_2–]_2$ (25 g, 151 mmol) in ethanol (300 cm^3) was stirred under dinitrogen at room temperature during the addition of small pieces of sodium metal (25 g, 1.09 mol) over a period of 2 h. The slurry dissolved after *ca.* half the sodium had been added. The mixture was heated at 70 °C for 4 h, and after cooling to room temperature water (300 cm^3) was added. The product was extracted with dichloromethane (4 × 200 cm^3), the extracts dried with anhydrous $MgSO_4$, and the solvent removed with a rotary evaporator to leave a pale yellow oil. The product was distilled *in vacuo* (b.p. 94—96 °C, 0.7 mmHg) to give a colourless oil (10 g, 57.5 mmol, 34%). ^1H N.m.r. ($CDCl_3$): 1.40 (4 H, br), 2.26 (6 H, s), 2.45 (4 H, t), 2.52 (4 H, s), and 2.78 p.p.m. (4 H, t). Electron-impact mass spectrum (Found: *m/z* 174; calc. for M^+, 174).

Preparation of L^1. The high-dilution technique was used to condense $[NH_2CH_2CH_2N(Me)CH_2–]_2$ with pyridine-2,6-dicarboxylic acid dichloride. A dry 5-dm^3 three-necked flask was evacuated and filled with dry dinitrogen (3 times) and then dry toluene (2 dm^3) and triethylamine (10 g, 99 mmol) were added. Two 50-cm^3 syringes were connected to the flask *via* long stainless steel needles passing through a rubber Suba-seal plug in one neck of the flask. The syringes were connected to a motor driven syringe pump (Sage instrument model 355) to allow controlled slow addition of the two reagents. The flask was connected to a magnetic stirrer, and cooled with an ice-bath to 0 °C. The two syringes were charged separately with solutions of $[NH_2CH_2CH_2N(Me)CH_2–]_2$ (8.5 g, 48.9 mmol) and pyridine-2,6-dicarboxylic acid dichloride (9.97 g, 48.9 mmol), each dissolved in dry toluene (50 cm^3). The reagents were pumped into the flask dropwise, with vigorous stirring, at a flow rate of 0.0774 cm^3 min^{-1}. After complete addition (11 h), stirring was continued for a further 11 h. The triethylamine hydrochloride which precipitated was removed by filtration, and the solution evaporated with a rotary evaporator. The remaining paste was

Table 2. ^{13}C N.m.r. chemical shifts (δ/p.p.m., reference $SiMe_4$) at 298 K in CD_3NO_2 solution unless specified otherwise (relative populations in parentheses)

		Pyridine (py) C			py–CH_2–N	N–CH_2–C			N–CH_3	
Compound	Isomer	*ortho*	*para*	*meta*						
L^1 [a]		148.54 (2)	138.94 (1)	123.72 (2)		57.40 (2)	56.78 (2)	36.36 (2)	38.73 (2)	
L^2		158.89 (2)	138.12 (1)	121.41 (2)	58.29 (2)	56.15 (2)	54.15 (2)	47.74 (2)	42.58 (2)	
$[Zn(L^2)(dmso)][ClO_4]_2$ [b]	Symmetric	155.84 (2)	143.64 (1)	123.55 (2)	56.38 (2)	55.73 (2)	50.01 (2)	48.89 (2)	46.19 (2)	
	Asymmetric	155.93 (1)	142.98 (1)	123.39 (1)	58.75 (1)	53.79 (1)	52.77 (1)	51.58 (1)	45.70 (1)	
		155.11 (1)		122.93 (1)	54.87 (1)	51.39 (1)	49.91 (1)	49.18 (1)	43.76 (1)	
L^3		158.80 (2)	137.72 (1)	123.78 (2)	63.52 (2)	54.58 (2)	53.82 (2)	53.36 (2)	44.09 (2)	43.96 (2)
$[Zn(L^3)][ClO_4]_2$	Symmetric	155.70 (2)	144.53 (1)	125.00 (2)	59.51 (2)	56.02 (2)	53.72 (2)	53.10 (2)	46.98 (2)	46.39 (2)
	Asymmetric	155.70 (2) [c]	144.53 (1) [c]	125.98 (1)	59.05 (1)	58.26 (1)	57.93 (1)	57.24 (1)	46.39 (1)	44.98 (1)
				126.21 (1)	55.79 (1)	55.79 (1)	55.53 (1)	50.01 (1)	44.29 (1)	43.59 (1)

[a] In $CDCl_3$; carbonyl resonance at δ 163.17 p.p.m. [b] At 253 K; co-ordinated dmso at δ 40.0 p.p.m. [c] Overlapping resonances, tentative assignment.

Table 3. U.v.–visible spectra of the complexes of Ni^{2+} and Cu^{2+} with L^2 and L^3 in solution, and their magnetic moments in the solid phase

		$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})		
Complex	Colour	In CH_3NO_2	In dmso	$\mu_{eff.}$
$[Ni(L^2)(dmso)][ClO_4]_2$	Green	*ca.* 500 (sh), 830 (sh), 895 (32)	550 (13), 660 (13), 825 (sh), 893 (36)	3.10
$[Ni(L^3)(dmso)][ClO_4]_2 \cdot H_2O$	Green	555 (16), 620 (sh), 930 (28)	602 (14), 680 (14), 830 (sh), 975 (31)	3.05
$[Cu(L^2)][ClO_4]_2$	Blue	612 (239), 908 (120)	612 (208), 910 (85)	1.93
$[Cu(L^3)][ClO_4]_2$	Blue	626 (287), 894 (132)	640 (227), 925 (95)	1.93

Table 4. Comparison of parts of the f.a.b. mass spectra of metal complexes of L^2 and L^3 with values calculated for the fragment ions $[M(L)ClO_4]^+$ and $[M(L - H)]^+$ (M = Ni, Cu, or Zn; L = L^2 or L^3)

	$[Ni(L^2)ClO_4]^+$					$[Ni(L^2 - H)]^+$			
Obs. *m/z*	434	435	436	437		334	335	336	337
Relative height	100	24	62	18		100	72	44	29
Calc. *m/z*	434	435	436	437		334	335	336	337
Relative height	100	19	73	16		100	19	40	9
	$[Cu(L^2)ClO_4]^+$					$[Cu(L^2 - H)]^+$			
Obs. *m/z*	439	440	441			339	340	341	342
Relative height	100	46	85			100	99	54	32
Calc. *m/z*	439	440	441			339	340	341	342
Relative height	100	8	79			100	19	46	9
	$[Zn(L^2)ClO_4]^+$					$[Zn(L^2 - H)]^+$			
Obs. *m/z*	440	442	444			340	341	342	
Relative height	100	55				100	36	86	
Calc. *m/z*	440	442	444			340	341	342	
Relative height	100	55				100	19	58	
	$[Ni(L^3)ClO_4]^+$					$[Ni(L^3 - H)]^+$			
Obs. *m/z*	462	463	464	465		362	363	364	365
Relative height	100	30	72	27		100	32	40	39
Calc. *m/z*	462	463	464	465		362	363	364	365
Relative height	100	22	74	17		100	21	41	10
	$[Cu(L^3)ClO_4]^+$					$[Cu(L^3 - H)]^+$			
Obs. *m/z*	467	468	469	470	471	367	368	369	370
Relative height	100	23	45	24	31	100	11	23	50
Calc. *m/z*	467	468	469	470	471	367	368	369	370
Relative height	100	22	80	17	17	100	21	47	10
	$[Zn(L^3)ClO_4]^+$					$[Zn(L^3 - H)]^+$			
Obs. *m/z*	468	469	470	471	472	368	369	372	
Relative height	100	17	91	26	51	100	62	65	
Calc. *m/z*	468	469	470	471	472	368	369	372	
Relative height	100	13	91	28	61	100	21	41	

dissolved in dichloromethane (50 cm^3), and the solution passed through a column of neutral alumina (20 × 2 cm diameter) and eluted with more dichloromethane (100 cm^3). After removal of the solvent with a rotary evaporator, the product was obtained as a white solid (3.59 g, 11.8 mmol, 24% yield), m.p. 155—156 °C. ^1H N.m.r. ($CDCl_3$): 2.20 (6 H, s), 2.60 (4 H, s), 2.73 (4 H, t), 3.54 (4 H, q), 8.05 (1 H, t), 8.30 (2 H, d), and 9.14 p.p.m. (2 H, br). Electron-impact mass spectrum (Found: *m/z* 305; calc. for M^+, 305). The ^1H-decoupled ^{13}C n.m.r. chemical shifts are given in Table 2).

Preparation of L^2. L^1 (1.1 g, 3.6 mmol) was dissolved in dry thf (100 cm^3) in a 250-cm^3 round-bottomed flask. The flask was flushed with dry dinitrogen, and a solution of $BH_3 \cdot thf$ (45 cm^3 of a 1.0 mol dm^{-3} solution) added. The solution was refluxed under dinitrogen for 3 h. Excess $BH_3 \cdot thf$ was then destroyed by the dropwise addition of methanol, and the solvent removed with a rotary evaporator to give the borane salt of L^2 as a white solid. This salt was dissolved in a mixture of water (50 cm^3) and methanol (50 cm^3), and concentrated HCl (30 cm^3) was added. The solution was refluxed overnight, and the pH then adjusted to *ca.* 12 by adding sodium hydroxide. The product was extracted with dichloromethane (4 × 100 cm^3), the extracts dried with anhydrous $MgSO_4$, filtered and evaporated to leave L^2 as a pale yellow oil. This oil was purified by passage through a neutral alumina column as described for L^1, using dichloromethane as eluant. The final yield was 83%. ^1H N.m.r. ($CDCl_3$): 2.20 (6 H, s), 2.48 (4 H, s), 2.60 (4 H, t), 2.72 (4 H, t), 3.92 (4 H, s), 4.40 (2 H, br), 7.05 (2 H, d), and 7.58 p.p.m. (1 H, t). Electron-impact mass spectrum (Found: *m/z* 277; calc. for M^+, 277). The ^1H-decoupled ^{13}C n.m.r. chemical shifts are given in Table 2.

Preparation of L^3. L^2 (0.9 g, 3.25 mmol) was added to 37% aqueous formaldehyde (10 cm^3) followed by formic acid (10 cm^3). The mixture was refluxed overnight at 90 °C, cooled to room temperature, basified with 20% aqueous NaOH to pH 12, and extracted with dichloromethane (5 × 100 cm^3). Work-up was as described for L^2, using dichloromethane–methanol (4:1, 200 cm^3) to elute from the alumina column. The product was obtained as a pale yellow oil (0.87 g, 2.85 mmol, 88%). ^1H N.m.r. ($CDCl_3$): 2.25 (12 H, s), 2.45 (12 H, m), 3.71 (4 H, s), 7.20 (2 H, d), and 7.61 p.p.m. (1 H, t). Electron-impact mass spectrum (Found: *m/z* 305; calc. for M^+, 305). The ^{1}H-decoupled ^{13}C n.m.r. chemical shifts are given in Table 2.

Preparation of metal complexes of L^2 *and* L^3. These were obtained in *ca.* 50—70% yields by adding a solution of each ligand (0.5 mmol) in ethanol (5 cm^3) to an equimolar amount of the appropriate metal dimethyl sulphoxide (dmso) solvates of formula $[M(dmso)_n][ClO_4]_2$ (M = Ni or Cu, $n = 6$; M = Zn, $n = 4$; prepared as described[8]) in ethanol (10 cm^3). The mixtures were stirred for 1 h, whereupon the solid products separated. These were collected by filtration and in some cases recrystallised from mixtures of nitromethane, ethanol, and diethyl ether using the solvent ratios indicated in Table 1. The products were finally washed with ethanol (2 × 5 cm^3) and diethyl ether (3 × 5 cm^3). The yields and elemental analyses are collected in Table 1. Proton-decoupled ^{13}C n.m.r. chemical shifts of the diamagnetic Zn^{2+} complexes are compared with those of the free ligands in Table 2, and details of the visible spectra and magnetic moments of the Ni^{2+} and Cu^{2+} complexes are in Table 3. Parts of the fast atom bombardment (f.a.b.) mass spectra of the complexes of L^2 and L^3 are compared with calculated values in Table 4.

Crystal Structure Analysis for $[Zn(L^3)][ClO_4]_2$.—Crystals of $C_{17}H_{31}Cl_2N_5O_8Zn$ suitable for crystallography were obtained as white plates from nitromethane solution. A crystal with dimensions 0.30 × 0.12 × 0.13 mm was chosen. Systematic absences *h*0*l*, $h + l \neq 2n$, and 0*k*0, $k \neq 2n$, indicated the monoclinic space group $P2_1/n$; $M = 569.74$, $a = 9.935(3)$, $b = 15.603(4)$, $c = 15.202(3)$ Å, $\beta = 94.30(2)°$, $U = 2\,349(1.0)$ A^3, $Z = 4$, $D_c = 1.61$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 13.48 cm^{-1}, $T = 290$ K, $F(000) = 1\,183.76$.

Data were collected with a maximum 2θ of 45°, scan range ±0.9° (2θ) around $K_{\alpha1}$–$K_{\alpha2}$ and with a scan speed of 2.5—29° min^{-1}, depending on the intensity of a 2-s pre-scan. Backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by a least-squares fit to 15 reflections with $18 < 2\theta < 20°$. Reflections were processed using profile analysis to give 3 380 unique reflections; 1 816 with $[I/\sigma(I) \geqslant 3.0]$ were used in refinement, and corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method. Heavy atoms were located by the Patterson interpretation section of SHELXTL, and light atoms found by successive Fourier syntheses. Anisotropic thermal parameters were used for all of the non-hydrogen atoms. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2, inserted at calculated positions, and not refined. Methyl groups were treated as rigid CH_3 units, with their initial orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. Final refinement was on *F* by cascaded least-squares methods, refining 310 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of heights +0.3 and −0.2 e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma(F)^2 + gF^2]$ with $g = 0.000\,15$ was used, and shown to be satisfactory by a weight analysis. The final *R* value was 0.0394 ($R' = 0.0361$). In the final cycle the maximum shift to error ratio was 0.03. Scattering factors in the analytical form and anomalous dispersion factors were taken from International Tables.[9] Final atomic co-ordinates are given in Table 5, and selected bond lengths and angles in Table 6.

Table 5. Atomic co-ordinates (× 10^4) for $[Zn(L^3)][ClO_4]_2$

Atom	*x*	*y*	*z*
Zn	2 308.3(7)	6 966.5(4)	6 067.7(4)
Cl(1)	2 725.3(17)	8 822.7(11)	8 455.6(10)
Cl(2)	2 427.3(19)	5 263.7(11)	1 704.7(12)
O(1)	2 434(6)	8 728(4)	7 559(3)
O(2)	3 305(6)	9 632(3)	8 653(4)
O(3)	3 652(6)	8 165(3)	8 735(4)
O(4)	1 553(7)	8 735(4)	8 880(5)
O(5)	3 494(5)	5 110(3)	1 146(3)
O(6)	2 826(8)	5 894(4)	2 320(4)
O(7)	1 296(6)	5 522(4)	1 176(4)
O(8)	2 171(6)	4 494(4)	2 139(4)
N(1)	2 246(5)	6 550(3)	7 307(3)
N(2)	104(4)	7 067(3)	6 271(3)
N(3)	1 985(5)	8 099(3)	5 387(3)
N(4)	2 723(5)	6 387(3)	4 874(3)
N(5)	4 495(5)	6 677(3)	6 449(3)
C(1)	3 291(6)	6 139(4)	7 698(4)
C(2)	3 279(7)	5 850(4)	8 551(4)
C(3)	2 155(7)	5 996(4)	8 995(4)
C(4)	1 056(7)	6 409(4)	8 568(4)
C(5)	1 132(6)	6 697(4)	7 729(4)
C(6)	74(6)	7 235(4)	7 233(4)
C(7)	−680(7)	6 286(4)	6 047(4)
C(8)	−390(6)	7 808(4)	5 728(4)
C(9)	707(6)	8 486(4)	5 667(4)
C(10)	3 079(7)	8 748(4)	5 503(4)
C(11)	1 840(7)	7 807(4)	4 439(4)
C(12)	2 880(7)	7 136(4)	4 282(4)
C(13)	1 693(7)	5 789(4)	4 472(4)
C(14)	4 014(6)	5 904(4)	5 033(4)
C(15)	5 066(6)	6 384(4)	5 638(4)
C(16)	5 319(7)	7 377(4)	6 877(5)
C(17)	4 400(6)	5 968(4)	7 098(4)

Table 6. Bond lengths (Å) and selected bond angles (°) in $[Zn(L^3)][ClO_4]_2$

Zn–N(1)	1.999(4)	Zn–N(2)	2.240(5)
Zn–N(3)	2.061(5)	Zn–N(4)	2.095(5)
Zn–N(5)	2.252(5)	Cl(1)–O(1)	1.379(5)
Cl(1)–O(2)	1.411(5)	Cl(1)–O(3)	1.423(6)
Cl(1)–O(4)	1.380(7)	Cl(2)–O(5)	1.428(5)
Cl(2)–O(6)	1.394(6)	Cl(2)–O(7)	1.392(6)
Cl(2)–O(8)	1.403(6)	N(1)–C(1)	1.322(7)
N(1)–C(5)	1.340(8)	N(2)–C(6)	1.489(7)
N(2)–C(7)	1.473(8)	N(2)–C(8)	1.481(7)
N(3)–C(9)	1.496(8)	N(3)–C(10)	1.485(8)
N(3)–C(11)	1.508(7)	N(4)–C(12)	1.490(7)
N(4)–C(13)	1.483(8)	N(4)–C(14)	1.492(8)
N(5)–C(15)	1.468(8)	N(5)–C(16)	1.485(8)
N(5)–C(17)	1.489(8)	C(1)–C(2)	1.375(8)
C(1)–C(17)	1.506(9)	C(2)–C(3)	1.366(10)
C(3)–C(4)	1.386(9)	C(4)–C(5)	1.360(8)
C(5)–C(6)	1.504(8)	C(8)–C(9)	1.527(8)
C(11)–C(12)	1.502(9)	C(14)–C(15)	1.535(9)
N(1)–Zn–N(2)	78.1(2)	N(1)–Zn–N(3)	137.5(2)
N(2)–Zn–N(3)	83.8(2)	N(1)–Zn–N(4)	134.3(2)
N(2)–Zn–N(4)	114.0(2)	N(3)–Zn–N(4)	88.2(2)
N(1)–Zn–N(5)	77.8(2)	N(2)–Zn–N(5)	155.9(2)
N(3)–Zn–N(5)	114.4(2)	N(4)–Zn–N(5)	83.6(2)

Results and Discussion

Ligand Syntheses.—Previous syntheses of pyridyl-containing penta-azamacrocycles have mainly used template methods,[1–6] although Kimura *et al.*[10] obtained a 16-membered ring diamide macrocycle, in unspecified yield, from refluxing (3 d) the diethyl ester of pyridine-2,6-dicarboxylic acid and 3,7-diazanonane-1,9-diamine in ethanol solution. In this study, the high-dilution method gave the 15-membered ring diamide macrocycle L^1 in 24% yield, in a rapid reaction between pyridine-2,6-dicarboxylic

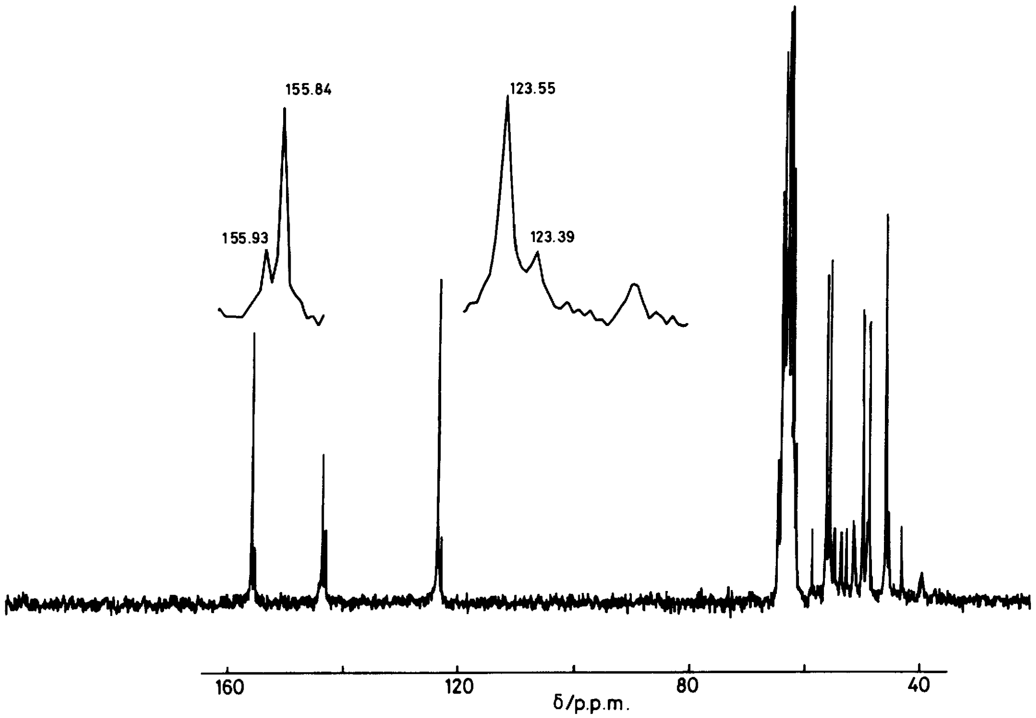


Figure 1. Proton-decoupled ^{13}C n.m.r. spectrum of $[Zn(L^2)(dmso)][ClO_4]_2$ in CD_3NO_2 solution

acid dichloride and 3,6-dimethyl-3,6-diazaoctane-1,8-diamine. The synthesis requires the use of an open-chain amine in which only the terminal amino-groups are capable of being attacked by the diacid chloride (*i.e.* R^2 in L^1 must be alkyl or aryl, and not hydrogen). Reduction of the amide groups of L^1 to give L^2 proceeds in good yield (> 80%) using BH_3·thf, and methylation of the secondary amine groups of L^2 with formaldehyde–formic acid gives L^3 in *ca.* 88% yield. The ligands were characterised by their ^1H n.m.r. and mass spectra, ^{13}C n.m.r. chemical shifts (Table 2), and by the analytical data for their metal complexes (Table 1).

Metal Complexes of L^2 *and* L^3.—These were obtained in good yields from the 1:1 reactions of the appropriate ligand and the dimethyl sulphoxide (dmso) solvates of each metal perchlorate in ethanol solution. Analytical data (Table 1) indicate the formation of either six-co-ordinate monosolvento complexes of formula $[M(L)(dmso)][ClO_4]_2$ ($L = L^2$ or L^3, $M = Ni$; $L = L^2$, $M = Zn$), or five co-ordinate complexes of formula $[M(L)][ClO_4]_2$ ($L = L^2$ or L^3, $M = Cu$; $L = L^3$, $M = Zn$). The visible spectra and magnetic moments of the Ni^{2+} and Cu^{2+} complexes (Table 3) are consistent with the formulations. The fast atom bombardment (f.a.b.) mass spectra of the complexes (Table 4) gave clusters of peaks as expected for the ions $[M(L)ClO_4]^+$ and $[M(L - H)]^+$ (M = Ni, Cu, or Zn). This behaviour is as expected from our earlier studies.[11,12] The f.a.b. spectrum of $[Zn(L^3)][ClO_4]_2$ also showed a strong peak assigned to $[H_2L^3(ClO_4)]^+$. This unexpected behaviour may indicate that the zinc(II) complex is the least stable of the three.

The ^{13}C n.m.r. spectrum of $[Zn(L^2)(dmso)]^{2+}$ in CD_3NO_2 solution is shown in Figure 1. It reveals the presence of a co-ordinated dmso molecule as a broad resonance at δ 40.0 p.p.m., broadening presumably being due to chemical exchange. The existence of a *ca.* 2:1 mixture of two isomers, one symmetric and the other asymmetric, is evident from the number of resonances in the spectrum; the assignments for the two isomers are given in Table 2. The presence of two isomers is also apparent in the ^{13}C n.m.r. spectrum of the $[Zn(L^3)]^{2+}$ ion, although only *ca.* 10% of the asymmetric isomer is present in this case (Table 2). Previous studies of pyridyl-containing penta-azamacrocycles have revealed three modes of co-ordination, (I)—(III), shown schematically in Figure 2. With saturated macrocyclic rings, seven-co-ordinate pentagonal-bipyramidal complexes, (I), are formed by Mn^{2+} and Fe^{3+}, and six-co-ordinate pseudo-octahedral complexes, (II), are formed by Co^{3+}, Ni^{2+}, and Cu^{2+} ions, in which unidentate anions or solvent molecules occupy the remaining co-ordination sites.[5,6,10] A structure of type (II) is reported for the Ni^{2+} and Co^{3+} complexes of 1,4,7,10,13-penta-azacyclohexadecane.[13] Pentagonal-bipyramidal Schiff-base complexes are also well known, including a

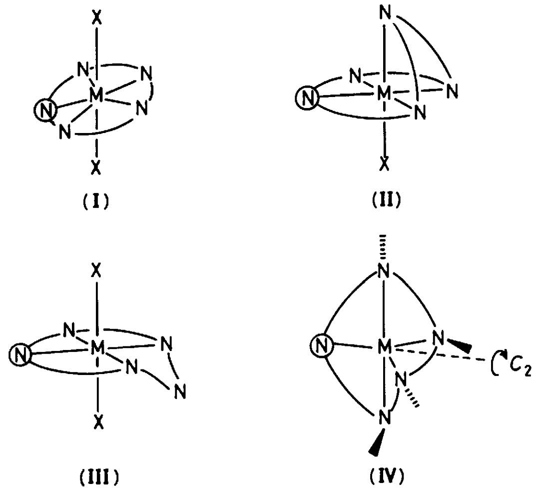


Figure 2. Schematic representation of the different modes of co-ordination found in metal complexes of L^1—L^5 (X = unidentate ligand, M = metal ion). The pyridine N atom is circled

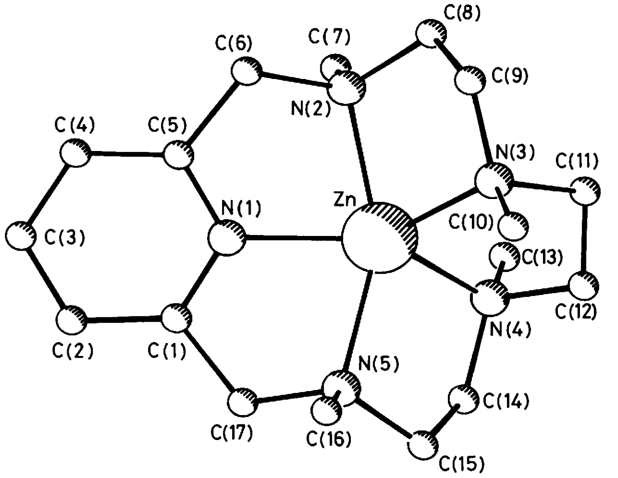


Figure 3. View of the symmetric isomer of $[Zn(L^3)]^{2+}$, showing the atomic numbering. Hydrogen atoms are omitted for clarity

complex of Zn^{2+}.[14] A structure in which one of the N atoms is unco-ordinated in a *trans*-octahedral arrangement of type (**III**) is also postulated for a low-spin Schiff-base macrocyclic complex of Fe^{2+} with cyanide ions occupying the axial positions.[15] Five-co-ordinate structures can also be envisaged for these penta-azamacrocycles, in which the macrocycle either occupies the corners of a square pyramid [analogous to structure (**II**) but with no axial unidentate ligand], or in a trigonal-bipyramidal mode as shown in structure (**IV**). In both modes of five-co-ordination the expected planarity of the metal ion with the pyridine N atom and the two flanking N atoms is maintained. There are, of course, many isomers of these structures possible, depending on the different chiralities of the N–H and N–Me groups. A symmetric structure observed in the ^{13}C n.m.r. spectra of the Zn^{2+} complexes is possible for structure (**IV**) with the N substituents arranged as shown. In this structure there is a C_2 rotation axis passing through the metal and pyridine N atoms, and bisecting the macrocyclic C–C bond furthest removed from the pyridine ring. The asymmetric species observed in the ^{13}C n.m.r. spectra could have either a square-pyramidal structure, or a non-symmetric structure (**IV**) with one of the chiral N atoms inverted.

Crystal Structure.—To gain further insight into the structure of the Zn^{2+} complexes, the crystal structure of $[Zn(L^3)][ClO_4]_2$ was determined. The cation geometry is shown in Figure 3. This can be equated to structure (**IV**), with a non-crystallographic C_2 rotation axis passing through Zn, N(1), and C(3). Such a symmetric isomer gives a satisfactory explanation for the major component identified from the ^{13}C n.m.r. spectrum in nitromethane solution. The MeN groups at positions 3 and 9 [N(2) and N(4)] are on the opposite side of the macrocycle to those at positions 6 and 12 [N(3) and N(5); Figure 3]. Major distortions from the idealised trigonal-bipyramidal geometry depicted in structure (**IV**) are apparent from the bond lengths and angles in Table 6. The 'axial' N(2)–Zn–N(5) angle is only 155.9(2)°, and the other N–Zn–N bond angles involving N(2) and N(5) are in the range 78.1(2)—114.0(2)°. The 'in-plane' N–Zn–N bond angles involving N(1), N(3), and N(4) are 137.5(2) and 134.3(2)° to the pyridine N atom [N(1)], and only 88.2(2)° for N(3)–Zn–N(4). However, the 'axial' Zn–N bond lengths (2.24 and 2.25 Å) are significantly longer than the 'equatorial' bond lengths (*ca.* 2.0—2.1 Å) as expected for a trigonal bipyramid. A very similar five-co-ordinate structure is reported for the $[Cu(L^4)]^{2+}$ ion, although in the copper(II) complex further distortions are apparent, attributable to the Jahn–Teller effect, which result in a structure between that of a square pyramid and a trigonal bipyramid.[16] For $[Zn(L^3)]^{2+}$ the structure is closer to that of a trigonal bipyramid than a square pyramid; for compounds showing square-pyramidal geometry, the N–metal–N bond angles are observed to have a characteristic pattern of four nearly equal and large values (usually *ca.* 135°), rather than having one angle much larger than the others, and the bond lengths are more nearly equal.[16]

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